

# THE ANALYST.

JULY, 1902.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A SPECIAL general meeting of the Society was held in the Chemical Society's rooms, Burlington House, on Wednesday evening, May 21, when a discussion took place on the Report of the Joint Committee appointed by the Society of Chemical Industry and the Society of Public Analysts to consider the question of the determination of minute quantities of arsenic. Sir William Church and Dr. G. S. Buchanan, of the Royal Commission on Arsenical Poisoning, Mr. Graham Aldous, and a number of members of the Society of Chemical Industry, were present. The President (Dr. J. Augustus Voelcker, M.A., B.Sc.) occupied the chair.

The minutes of the previous meeting having been read and confirmed, a certificate of proposal for election to membership in favour of Mr. Alfred Howard, A.R.C.S., A.R.S.M., was read for the second time.

The monthly meeting of the Society was held on Wednesday evening, June 4, in the Chemical Society's rooms, Burlington House. The President (Dr. J. Augustus Voelcker, M.A., B.Sc.) occupied the chair.

The minutes of the previous meeting were read and confirmed.

A certificate of proposal for election to membership in favour of Mr. Peter Macdonald, Apartado No. 17, Saltillo, Mexico, assayer to the Mazapil Copper Co., Mexico, was read for the first time.

Messrs. M. Wynter Blyth, Alfred Howard, and Walter F. Sutherst were elected members of the Society.

The following papers were read: "Note on the Examination of Water from some Typhoid-polluted Wells," by S. Rideal, D.Sc.; "The Estimation of Platinum in Alloys," by Percy A. E. Richards; "The Electrolytic Detection and Estimation of Arsenic," by E. J. Bevan; and "The Action of boiling Hydrochloric Acid on Arsenic Acid," by Otto Hehner.

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DISCUSSION ON THE REPORT OF THE JOINT COMMITTEE OF THE  
SOCIETY OF CHEMICAL INDUSTRY AND PUBLIC ANALYSTS ON  
THE DETERMINATION OF MINUTE QUANTITIES OF ARSENIC.

*(Held at the Meeting, May 21, 1902.)*

AFTER some preliminary remarks by the President, Mr. HEHNER, Chairman of the Joint Committee of the two Societies, stated that it had been found that the process of purification of hydrochloric acid prescribed by the Committee, although fully answering in the majority of cases, had not been infallible in freeing acid from arsenic.

It had been found that it was better not to dilute the acid as prescribed, but to use the strong acid of commerce, to add bromine and an excess of sulphurous acid to it, and to distil off and reject about one-fifth, the remainder of the distillate being then perfectly free from arsenic, even if crude yellow hydrochloric acid had been employed.

It had further been found that zinc could be freed from arsenic by treating it in its molten condition with sodium, and removing the sodium as completely as possible by subsequent air oxidation.

The discussion was opened by Dr. THOMAS STEVENSON, who thought the mode of purification of hydrochloric acid as recommended by the Committee somewhat too cumbrous, and expressed his opinion that, by distilling off a portion and taking the remainder, acid sufficiently free from arsenic could always be obtained. He further objected to the presence of the hydrobromic acid, as this might form free bromine, which might be a source of error. For the testing of commercial products he preferred the Reinsch method. He admitted that it was capable of detecting only one part of arsenic in three or four million parts, with a limit of about one-fiftieth of a grain per gallon in the case of beer. If arsenic were present in organic combination, neither the Reinsch nor the Marsh test would discover it, and in such cases the destruction of organic matter was a necessity.

Mr. ALLEN criticised the Committee's process of hydrochloric acid purification, and preferred oxidizing any arsenic which might be present by potassium permanganate or bichromate of potash, and distilling, rejecting the first small portion. The different methods of sulphuric acid purification answered, he thought, well. It was a matter of considerable trouble to obtain zinc answering all requirements, and he expressed his strong conviction that a small quantity of iron must be present with it in order to give an equal flow of hydrogen gas and a comparable brown mirror. At the same time, the presence of too much iron must be avoided, or the zinc becomes insensitive.

Mr. A. R. LING, referring to Dr. Stevenson's censure of the method of purifying hydrochloric acid, pointed out that pure hydrochloric acid was liable to contain free chlorine. As regards the treatment of zinc by means of sodium, it was very important to remove all the sodium, preferably by baking the zinc in a muffle.

Mr. R. BODMER had failed to obtain indications of arsenic both by the Marsh

and Reinsch methods in the case of cacodylates. He had also failed to obtain good results with the Committee's basic process for destruction of the organic matter.

Mr. JULIAN BAKER referred to the difficulty of testing the dust from malt-kilns, and recommended that these should always be burnt with lime, and then tested by the Marsh process, and not directly.

Mr. WOOD-SMITH gave his opinion that the Committee's process was the only practicable one, and he considered that the use of the Reinsch process was fraught with danger to the brewer.

Dr. L. T. THORNE gave a description of his process for purifying hydrochloric acid,\* already described by him to the Chemical Society. He had found that, starting with good zinc, one treatment with sodium was sufficient to remove all traces of arsenic. He had found no loss of sensitiveness, but gave the warning that no sodium should be left in the zinc. His experience was that with sugars he always obtained the same results with or without destruction of the organic matter. He considered the Marsh test to be infinitely preferable to the Reinsch.

Dr. P. SCHIDROWITZ thought the test to be, on the whole, a good one for all practical purposes. As regards the sensitiveness of either zinc or acid, he suggested that selenium might be one of the factors to be taken into consideration.

Dr. BERNARD DYER demurred somewhat to the small quantity of beer to be taken for the test. He preferred to employ a larger quantity. He used the Committee's process with hydrochloric acid for all sorting purposes, but in cases requiring further investigation he worked upon a quantity of 70 c.c. or more, destroying the organic matter by acid treatment.

Mr. BENJAMIN E. R. NEWLANDS pointed out that the basic method of destruction of organic matter had been devised by himself, and was the subject of a patent for the retention of arsenic in coke for malting purposes.

Mr. A. J. MURPHY preferred to ascertain approximately the amount of arsenic by the Committee's process, and then to run three parallel tests—one a blank, the second a blank with the addition of a quantity of arsenious acid corresponding with the result obtained in the first test, and the third with a known quantity of the substance to be tested, so that in every case he obtained a fresh standard for comparison.

Messrs. L. BRIANT and A. J. STAREY made suggestions bearing upon the heating of the tube and the cooling of that portion of it where the mirror was expected to be deposited.

Mr. HEHNER, in summing up, showed that, with one single exception, the members who had expressed their opinions had been unanimous in favour, at least, of the principle underlying the Joint Committee's method, and that the discussion had been mainly concerned with the consideration of small details, which in themselves did not seriously modify the method in question.

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\* See abstract, this number, p. 233.

## ALKALINE WATERS FROM THE LOWER GREENSAND.

BY W. W. FISHER, M.A., F.I.C.

*(Read at the Meeting, April 9, 1902.)*

IN a paper recently read before the Society entitled "On Alkaline Waters from the Chalk" it was pointed out that alkaline waters are obtained not only from the chalk where it is covered by thick beds of London clay and tertiaries, but also from other porous rocks similarly covered. (See ANALYST, August, 1901.)

Although abnormal chalk waters have often been discussed, little attention has been paid to similar waters in lower greensand or Portland beds underlying the gault, which belong to a much earlier epoch in geological history.

In those localities where the lower greensand is exposed it is very porous, and absorbs a large proportion of the rainfall, and yields generally good waters, many of which, containing little lime, are soft in character. In Table I. a few typical examples of such waters are given, from which it will be seen that the total solids are sometimes very small, with low figures for chlorides and saline constituents, the proportion of organic matter also being quite small. Notable quantities of nitrates are often present, and occasionally the proportion of iron is large and causes inconvenience.

Beneath the lower greensand, and practically continuous with it as regards water-bearing characters, are the Portland beds, which in Berks and Oxfordshire are often sandy in character, with occasional masses or beds of limestone rock. Typical waters from these beds are given in Table II., and it will appear that they do not differ in any important respect from other limestone waters. Inasmuch as a thick bed of Kimmeridge clay underlies the Portland beds, no water can percolate downwards, and in most localities water is easily obtained by wells of moderate depth.

In the counties of Oxford and Buckingham both the greensand and Portland beds, having a slight dip to the south-east, pass gradually beneath the gault clay, and considerable areas of these water-bearing strata are thus buried. Over these districts the water is obtained by borings often 200 feet in depth. The gault continues through Berkshire into Wiltshire, but only as a narrow strip, and where the greensand has been removed by denudation, and the Portland beds are absent, the gault lies directly upon the Kimmeridge clay, and for fifteen miles the two formations are in contact. Near Farringdon, Berks, the greensand reappears, but further west becomes narrow and of little importance in respect of water supply.

Opportunities have offered from time to time of examining waters obtained by borings through the gault, and the results of the analysis of some interesting samples are embodied in Table III., a more detailed account of the saline constituents being set out in Table IV. in respect of five samples.

These samples are materially different in character from those obtained from the uncovered beds; they contain considerable quantities of saline constituents, chiefly alkaline chlorides, sulphates, and carbonates; the proportion of nitrogen as nitrates is small, but, as in many deep-well waters, distinct amounts of ammonia are present.

If we compare the waters in Table IV. with each other very striking differences

TABLE I.—WATERS FROM THE LOWER GREENSAND (UNCOVERED GREENSAND).  
(Results in Grains per Gallon. 1 Gallon = 70,000 Grains.)

| No.  | Locality.         | Depth in Feet. | Total Solids. | Chlorine in Chlorides. | Nitrogen in Nitrates. | Saline Ammonia. | Albu-<br>menoid<br>Ammonia. | Oxygen ab-<br>sorbed, etc.<br>3 hours. | Total Hard-<br>ness. | Remarks.                 |
|------|-------------------|----------------|---------------|------------------------|-----------------------|-----------------|-----------------------------|----------------------------------------|----------------------|--------------------------|
| 1132 | Bagley,           | 25             | 19.3          | 0.9                    | .640                  | .004            | .003                        | .021                                   | 13.5                 |                          |
| 1269 | Boars Hill,       | 38             | 6.0           | 1.0                    | .210                  | 0               | .004                        | .013                                   | —                    | Soft.                    |
| 2046 | "                 | —              | 20.4          | 1.3                    | .396                  | .003            | .008                        | .007                                   | —                    |                          |
| 2190 | Faringdon,        | —              | 30.8          | 1.1                    | .85                   | .001            | .005                        | .012                                   | 19.1                 | Permanent hardness, 5.7. |
| 2582 | Near Faringdon,   | —              | 37.0          | 4.1                    | .07                   | .003            | .008                        | .018                                   | —                    | Hard.                    |
| 2583 | Uffington,        | —              | 28.0          | 2.9                    | .014                  | .030            | .012                        | .182                                   | —                    | Soft, contains iron.     |
| 2563 | Wantage,          | —              | 32.0          | 1.3                    | .385                  | .002            | .006                        | .013                                   | —                    | Hard.                    |
| 1341 | Shotover,         | —              | 10.6          | 1.4                    | .490                  | 0               | .001                        | 0                                      | —                    | Soft.                    |
| 2052 | "                 | Spring         | 19.9          | 1.6                    | .315                  | .003            | .007                        | .042                                   | —                    |                          |
| 1307 | Nuneham,          | —              | 17.3          | 1.5                    | .175                  | .001            | .006                        | .023                                   | —                    |                          |
| 2509 | "                 | 90             | 23.5          | 2.9                    | .210                  | .006            | .004                        | .019                                   | —                    | Soft.                    |
| 1859 | Clifton Hampden,  | —              | 24.0          | 1.4                    | .497                  | .001            | .005                        | .014                                   | —                    |                          |
| 2485 | Great Brickhill,  | Spring         | 14.0          | 1.2                    | .497                  | .003            | .001                        | .014                                   | —                    | Soft.                    |
| 1941 | Godalming, Surrey | "              | 20.4          | 1.2                    | .028                  | .003            | .001                        | .005                                   | 16.0                 | Contains a little iron.  |

TABLE II.—WATERS FROM THE PORTLAND BEDS (UNCOVERED).  
(Analysis in Grains per Gallon.)

| No.  | Locality.  | Depth in Feet. | Total Solids. | Chlorine in Chlorides. | Nitrogen in Nitrates. | Saline Ammonia. | Albu-<br>menoid<br>Ammonia. | Oxygen ab-<br>sorbed, etc.<br>3 hours. | Total Hard-<br>ness. | Remarks.                                             |
|------|------------|----------------|---------------|------------------------|-----------------------|-----------------|-----------------------------|----------------------------------------|----------------------|------------------------------------------------------|
| 2519 | Radley,    | 80             | 29.6          | 1.9                    | .014                  | .001            | .003                        | .011                                   | —                    | Hard.                                                |
| 1518 | Itley,     | —              | 32.0          | 1.0                    | .546                  | 0               | .003                        | .022                                   | —                    | "                                                    |
| 2363 | Cuddesdon, | —              | 56.0          | 1.2                    | .028                  | .003            | .009                        | .070                                   | —                    | Hard, excess CaSO <sub>4</sub> from Kimmeridge clay. |
| 1127 | Stowe,     | Spring         | 23.2          | 1.4                    | .154                  | 0               | .012                        | .043                                   | 18.0                 |                                                      |
| 1969 | Brierton,  | 12             | 38.0          | 1.8                    | .532                  | 0               | .006                        | .030                                   | —                    | Hard.                                                |
| 2082 | Quanton,   | Spring         | 27.2          | 1.0                    | .448                  | .001            | .003                        | 0                                      | 22.6                 | "                                                    |

TABLE III.—WATERS FROM LOWER GREENSAND (OR PORTLAND BEDS) BELOW GAULT CLAY.  
(Analysis in Grains per Gallon.)

| No.  | Locality.          | Depth in Feet. | Total Solids. | Chlorine in Chlorides. | Nitrogen in Nitrates. | Saline Ammonia. | Albu-<br>menoid<br>Ammonia. | Oxygen ab-<br>sorbed, etc.<br>3 hours. | Total Hard-<br>ness. | Remarks.                        |
|------|--------------------|----------------|---------------|------------------------|-----------------------|-----------------|-----------------------------|----------------------------------------|----------------------|---------------------------------|
| 3008 | Warborough, Oxon   | 177            | 546.0         | 190.7                  | .05                   | .252            | .006                        | .044                                   | —                    | Water-level 6 ft. from surface. |
| 2749 | Newington, "       | 85(?)          | 414.0         | 148.5                  | .014                  | .072            | .003                        | .018                                   | —                    | " 40 ft. "                      |
| 2684 | Stadhampton, "     | 52             | 236.0         | 48.3                   | .021                  | .072            | .006                        | .124                                   | 32.9                 | " 47 ft. "                      |
| 3849 | Near Thame, "      | 96             | 77.2          | 12.1                   | .028                  | .037            | .003                        | .032                                   | 3.3                  | " 36 ft. "                      |
| 3743 | Wheatfield, "      | 211            | 79.0          | 9.7                    | .014                  | .028            | .005                        | .049                                   | 3.5                  | " 35 ft. "                      |
| 3801 | Cheddington, Bucks | 213            | 26.6          | 1.9                    | .014                  | .032            | .003                        | .024                                   | 9.7                  | " 113 ft. "                     |
| 3230 | Rowsham, "         | 12             | 95.0          | 2.5                    | .021                  | .005            | .005                        | .008                                   | Hard                 | " 3 ft. "                       |
| 3283 | Near Cambridge ... | 134            | 215.0         | 19.9                   | .014                  | .071            | .024                        | .160                                   | "                    | Excess CaSO <sub>4</sub>        |

TABLE IV. (Grains per Gallon.)

|                                 | No. ...<br>Locality | 3008<br>Warborough. | 2749<br>Newington. | 2684<br>Stadhampton. | 3849<br>Near Thame. | 3743<br>Wheatfield.                | 3801<br>Cheddington.               |
|---------------------------------|---------------------|---------------------|--------------------|----------------------|---------------------|------------------------------------|------------------------------------|
| Chlorine                        | ...                 | 190.7               | 148.5              | 48.3                 | 12.1                | 9.7                                | 1.9                                |
| Sulphuric acid, SO <sub>3</sub> | ...                 | 126.87              | 88.2               | —                    | 4.2                 | 4.66                               | 1.91                               |
| Carbon dioxide, CO <sub>2</sub> | ...                 | 4.80                | 7.3                | 6.7                  | 20.5                | 21.56                              | 8.08                               |
| Soda, Na <sub>2</sub> O         | ...                 | 241.19              | 188.0              | —                    | 40.3                | [48.65]                            | [4.16]                             |
| Magnesia, MgO                   | ...                 | 7.14                | 5.88               | —                    | .5                  | .50                                | 1.54                               |
| Lime, CaO                       | ...                 | 17.50               | 9.8                | —                    | .84                 | 1.40                               | 6.30                               |
| Silica, SiO <sub>2</sub>        | ...                 | 1.09                | —                  | —                    | .42                 | 2.1                                | 2.21                               |
|                                 |                     |                     |                    |                      |                     | Fe <sub>2</sub> O <sub>3</sub> .84 | Fe <sub>2</sub> O <sub>3</sub> .21 |
| Sodium chloride                 | ...                 | 314.25              | 244.7              | 79.3                 | 19.94               | 15.92                              | 3.13                               |
| Sodium sulphate                 | ...                 | 171.14              | 133.8              | —                    | 7.45                | 8.05                               | 3.38                               |
| Sodium carbonate                | ...                 | —                   | —                  | —                    | 45.30               | 48.22                              | 2.48                               |
| Magnesium sulphate              | ...                 | 8.20                | 17.48              | —                    | —                   | —                                  | —                                  |
| Magnesium carbonate             | ...                 | 9.19                | —                  | —                    | 1.05                | 1.07                               | 3.22                               |
| Calcium carbonate               | ...                 | —                   | 15.98              | —                    | 1.50                | 2.50                               | 11.25                              |
| Calcium sulphate                | ...                 | 42.50               | 2.07               | —                    | —                   | —                                  | —                                  |
| Total solids                    | ...                 | 546.37              | 414.04             | 236.0                | 77.28               | 79.0                               | 26.6                               |

may be noted. In the first pair from Warborough and Newington large quantities of sodium chloride and sulphate are present, with smaller quantities of magnesium and calcium salts. The solid residues were alkaline in reaction, but no free sodium carbonate was found. In the next pair of wells, about eight miles distant from the former, we find at Wheatfield and near Thame, although some sodium chloride and sulphate are present, sodium carbonate is the most abundant constituent. A third well near Thame yields water almost identical in composition, and I may mention that both the Thame wells have been under my observation for twenty years, and the waters have hardly changed in character during that period.

The boring at Cheddington, in Bucks, is about sixteen miles distant, and was only recently made, but the water is of special interest, as the alkaline constituents are much diminished in quantity, the total solids being remarkably less than in the other samples of similar origin. It is, however, a typical water of the class, and contains some sodium carbonate, as well as chloride and sulphate.

The explanations suggested at various times to account for soft alkaline waters in chalk have been discussed in my former paper, and need not be referred to again, except to point out that the view that the alkaline waters are derived from the sea by infiltration is clearly out of the question in respect of these samples. The hypothesis which was dismissed as untenable in respect of the chalk waters is still more improbable as an explanation of the peculiarities of lower greensand waters.

It seems beyond doubt that the mineral constituents of these waters are derived from the beds from which they are drawn—that is, from the greensand and Portland beds—and not from the clay or any other external source.

The exposed parts of these beds, as of other porous and permeable formations, have for long ages beyond reckoning been exposed to continual percolation, and by natural discharges from springs the more soluble constituents, especially the alkaline salts, have been eliminated. On the other hand, where such beds are covered by extensive clay deposits percolation must be slow and difficult, and, unless natural outlets exist, no removal of soluble salts can take place. It must further be remembered that most of these waters from borings in the gault have travelled long distances beneath the clay from their gathering grounds—possibly three or four miles—which means 15,000 or 20,000 feet of material to be traversed at an extremely slow rate, the conditions thus in the highest degree favouring the extraction of soluble matters.

Yet, accepting these considerations, it is not at first apparent why there should be such large differences between the Warborough, Wheatfield, and Cheddington samples, but a study of the surface contours suggests that they may arise from differences in level. We find that at Warborough, in the Thames Valley (close to the river), the surface level is 160 feet above Ordnance Datum, but at Wheatfield 257 feet (nearly 100 feet higher); while towards Cheddington the surface gradually rises to 342 feet at the site of the well, and even above 400 feet in the neighbourhood. Deducting the depth of boring (177 feet at Warborough), we find the bottom of the gault is 17 feet below sea-level at this locality, whereas at Wheatfield (the depth being 211 feet) the bottom of the clay and the top of the greensand is 46 feet above Ordnance Datum. The depth near Thame is probably much the same, while at Cheddington the

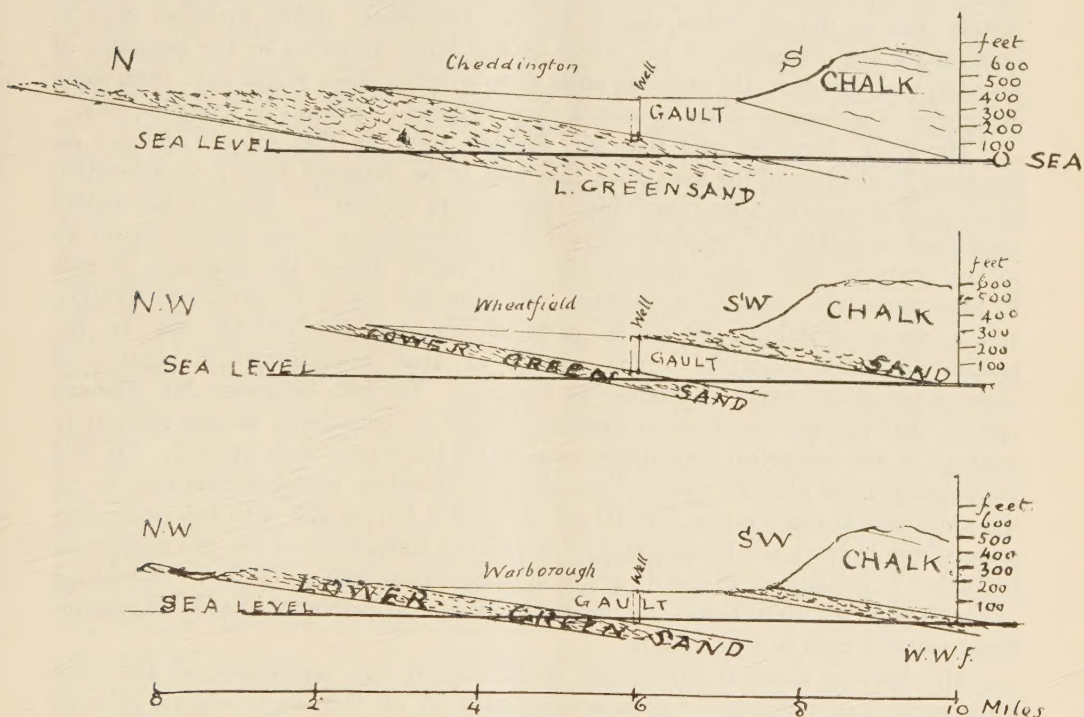
elevation similarly is 129 feet at the base of the clay. The greensand is full of water, which rises at all wells, and, taking the water-levels in Table III., we find the water surfaces respectively are 154 feet O.D., 222 feet O.D., and 229 feet above O.D. at Cheddington. Clearly this water may slowly travel along the slightly inclined strata, and escape by any natural outlet at a lower level where springs exist. The north-



western margin of the gault is in many places below this level, and an escape for the waters accordingly exists. At Warborough it is not possible for the buried waters to find a natural escape, but probably near Thame some discharge takes place, which even in limited quantity permits some movement onwards of the underground waters, and accounts for the intermediate character of the samples. It is

worthy of note that the Thames Valley is actually the lowest part of the gault which rises gradually through Berkshire until it reaches a considerable elevation.\*

I was fortunate in obtaining a specimen of a core from the lower greensand at Wheatfield for examination. It contained an appreciable quantity of sodium carbonate, with traces only of alkaline sulphate and chloride. When finely ground and thoroughly extracted with water, the sodium carbonate estimated by titration was 0.25 per cent. No evidence of the presence of silicate of soda was obtained in the aqueous solution.



Geological maps, superficial and sectional, of the district whence these waters were obtained are appended.

My best thanks are due to Mr. A. W. Ellis for his co-operation, and for most of the analyses of the mineral constituents of the deep-well waters.

The PRESIDENT having invited discussion,

Mr. F. J. LLOYD observed that the water from Uffington, No. 2583, seemed to be quite different from all the other waters referred to in Table I., and he would certainly think from the figures that that water was not free from contamination. The next question that arose in his mind was as to the source of these comparatively

\* A parallel case is found in Essex, where the waters from deep wells in chalk beneath the London clay are alkaline only where the chalk is much below Ordnance Datum, but calcareous when derived from the more elevated chalk under the clay in the northern parts of the county, and where natural drainage is accordingly possible.

large quantities of saline ammonia. It would appear, if the nitrates had been reduced to ammonia, that larger quantities of saline ammonia, with correspondingly smaller quantities of nitrates, would be found as the depth of the bed increased; and the figures given supported that view to a certain extent, but not altogether, because in the water from Cheddington (Table III.) the nitric nitrogen was only slightly less than that in the next sample, from Rowsham, although the water-level in the latter case was only 3 feet from the surface, as against 113 feet in the former case. Of course, it may have been that the beds were entirely different, although in the same county, but he did not think that there was sufficiently strong evidence here to account for the formation of the whole of the saline ammonia by the reduction of nitrates, and therefore the question arose as to whether there might have been some compound of ammonia—some ammonia-clay compound—present in the gault clay.

Mr. W. T. BURGESS said that Mr. Fisher's work on this subject afforded an excellent illustration of the assistance that was to be obtained from a consideration of the geological formations from which waters were derived. Some of the waters mentioned in Table III., containing very large quantities of total solids, would be in the ordinary way quite undrinkable. He could detect the presence of salt by taste when the quantity of chlorine just exceeded about 15 parts per 100,000, and a water containing 30 or 40 parts of chlorine per 100,000 was to his palate distinctly brackish. Such waters as that containing 190 grains of chlorine per gallon would be useless as a supply. He fully endorsed Mr. Fisher's opinion that the results of water analyses should be considered almost entirely in relation to the geological formations from which the waters were derived. He had examined several alkaline waters from the corresponding geological formations on the south side of the Thames, but did not remember having met with any (excluding waters from beneath the London clay) of so alkaline a character as the two mentioned in Table IV., containing 45 and 48 grains of carbonate of soda per gallon. Something under 30 parts per 100,000 was the highest proportion of carbonate of soda he remembered meeting with in such waters.

Mr. JENKINS asked if Mr. Fisher could suggest any explanation of the total disappearance of carbonate of soda accompanied by an increase in sodium chloride and in sodium sulphate in the case of the waters referred to in Table IV., as the beds went down towards the south-west.

The PRESIDENT (Dr. Voelcker) said that, in dealing with waters from the neighbourhood of Woburn, he had met with great variations in the quality of the water drawn from different springs. These variations, however, would be to a large extent explained by the facts which Mr. Fisher had put forward. The farm with which he was concerned was on the lower greensand formation, and it would be imagined that the waters obtained from the greensand itself would not be of a particularly hard nature, and would not contain large quantities of chlorides or sulphates; but, as a matter of fact, although in some parts of Buckinghamshire, just on the borders of Bedfordshire, such waters were met with as that at Great Brickhill (Table I.), which contained only 14 grains of total solids per gallon, nevertheless, the water obtained at the farm to which he was referring, only about three miles from Great Brickhill, contained large quantities of chlorides and sulphates. This constituted a consider-

able difficulty in the way of obtaining a suitable supply of water for the cottages and farms on the Bedford estate. He agreed with Mr. Lloyd in thinking that the Uffington water required some explanation; and the large quantity of saline ammonia in the sample from Warborough would lead one to wish for further knowledge in regard to that supply also. Possibly the explanation might lie in the fact that the water-level was only 6 feet from the surface.

Mr. FISHER, in reply, said that it seemed to him quite open to argument, on the figures of the analysis, whether the Uffington water was an entirely unpolluted sample. The water was obtained from a spot which the local authority had chosen in looking for a supply for the village. As was mentioned in the table, it contained iron, being, in fact, so highly ferruginous as to be unfit for the purpose for which it was intended. Although it was drawn from a porous formation, the quantity of nitrates in it was small. The saline ammonia may have been, and possibly was, due to the fact that the well had been only recently made for the purpose of proving the water. The quantity of oxygen absorbed was high, but, as the quantity of albuminoid ammonia was relatively moderate, the high quantity of oxygen absorbed might have been partly due to the presence of ferrous iron in the water. The question of the formation of ammonia by the reduction of nitrates was a complex one. The investigations of Professor Warington on the subject of denitrification by organisms were well known. Probably, however, there was not much bacterial life in existence at the depths in question. There might be some ammonia derived originally from organic remains in the clay which had never been washed out. It was not possible to explain entirely the origin of the ammonia, but the point he wished to insist upon was that, in these waters from great depths beneath beds of clay, ammonia was a constantly occurring constituent, while the quantity of nitrates present was small. The point mentioned by the President in regard to Woburn was, perhaps, to some extent capable of explanation by the fact that the drift-clay covered a considerable proportion of the estate, so that there could be no downward percolation, but only horizontal circulation. The Warborough sample obviously would not be fit to drink on account of its saline constituents. The boring, however, was a perfectly new one, and, although he could not say exactly where the ammonia came from, he did not think it likely that the water had become seriously contaminated.

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## THE DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF SULPHURETTED HYDROGEN IN COAL-GAS.

By W. J. DIBDIN, F.I.C., AND R. G. GRIMWOOD, F.I.C.

*(Read at the Meeting, April 9, 1902.)*

OWING to a recent proposal to modify the test for sulphuretted hydrogen as used on the London gas supply, it became necessary to ascertain, as no published data could be found on the point, what was the best means of estimating small quantities of sulphuretted hydrogen in coal-gas, and what degree of delicacy could be attained in its detection.

The apparently sensitive colour reaction between sodium nitro-prusside and an alkaline sulphide was examined, but it was found that the sensitiveness was more apparent than real, a much larger quantity than is ever likely to be present in purified coal-gas being required to produce any colour.

Recourse was therefore had to the coloration of lead salts, which is the system at present in use. Although it is well recognised that this reaction is a very delicate one, it is somewhat surprising to find how extraordinary its delicacy is; in fact, instead of there being any difficulty in detecting minute traces, the difficulty is to modify the test so that infinitesimal traces are not detected.

An attempt to produce a titrateable solution of a lead salt by passing through it gas containing sulphuretted hydrogen was unsuccessful, owing to the colour which was also produced by tarry matters in the gas. The coloration of paper soaked in a solution of a lead salt was next examined, papers soaked in various strengths of lead salts in solution being compared. From the results of this comparison it was decided to adopt a paper prepared by moistening with an approximately 12 per cent. solution of lead acetate, the paper whilst still wet being placed for a few minutes in an atmosphere of ammonia gas. Papers prepared in this way are used in London for testing the purity of the gas supply.

For several reasons it was found preferable to use these papers dry, considerable difficulty being found in distinguishing when the colour first appeared on a wet paper, and also because when wet they were unworkably sensitive.

The apparatus employed for preparing the sulphuretted hydrogen-contaminated gases consisted of a glass reservoir of known capacity, into which measured quantities of sulphuretted hydrogen could be introduced. As soon as the sulphuretted hydrogen had thoroughly diffused the contaminated gas was examined by expanding a toy balloon inside the reservoir, and thus forcing the gas through a small bore tube, so arranged that the gas as it issued from it impinged on a lead paper prepared as already described. The following illustration shows the apparatus employed.

The reservoir, the capacity of which is 15,500 c.c. when the balloon is deflated, is fitted at the neck with an I.R. stopper pierced with three holes, one fitted with a cock of sufficient bore to pass at least ten feet of coal-gas per hour under the ordinary gas-supply pressure; the second with a glass tube, reaching about one-third down the reservoir, to the end of which is fitted gas-tight an I.R. balloon capable of being expanded so as to fill the reservoir; and the third with a narrow bore glass tube leading to the apparatus where the examination is made.

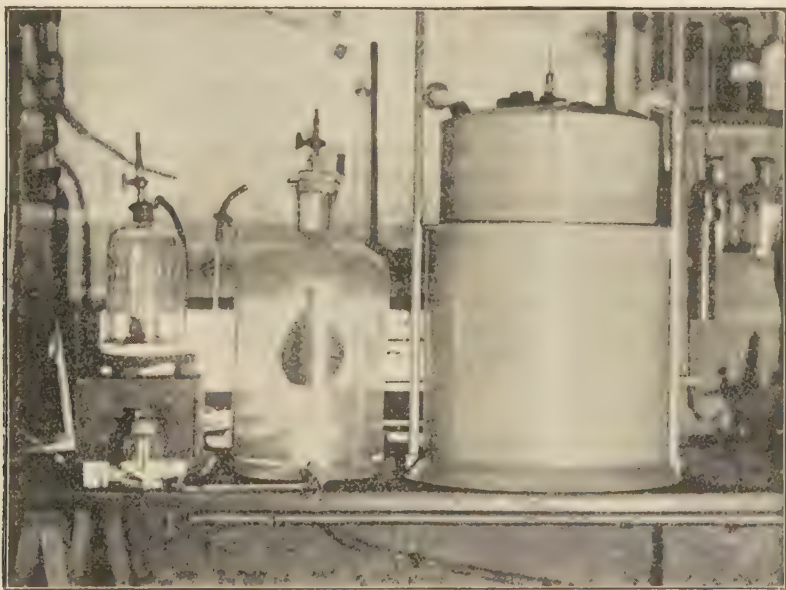
This consisted of a bell-jar standing in a mercury seal, and fitted at the top with a glass tube, which provides a secondary gas supply, and a cock and a burner, which gives a jet flame. By means of a cock or screw-clip on the inlet tube the height of the flame can be adjusted in this burner so that the gas burns at half a foot per hour.

At the bottom of the reservoir two tubes are fitted through an I.R. stopper, one of which connects with the gas-supply, and the other, which is of small bore, is fitted with a cock or clip.

To ascertain what amount of sulphuretted hydrogen could be detected in a coal-gas, a known volume of sulphuretted hydrogen was introduced through the capillary tube at the bottom of the reservoir, and allowed to diffuse through the gas. This, as

a rule, took from thirty to forty-five minutes. When diffusion was complete, the balloon was partially inflated, thus forcing some of the gas into the apparatus containing the lead paper, which was fixed in such a way that the gas impinged directly on it. In order to insure the thorough diffusion of the sulphuretted hydrogen a second test was always made with the apparatus connected to the bottom of the reservoir and the spots on the two slips of paper compared.

If sulphuretted hydrogen was in this way detected, a measured volume of the contaminated gas was withdrawn from the reservoir and the remainder washed out by a current of coal-gas, the gas being burnt from the cock at the top. As soon as the gas in the reservoir was free from sulphuretted hydrogen, the measured volume of contaminated gas was replaced, diffusion allowed to take place, and the contents again examined. By this means it was possible to detect, within a reasonable time,



one volume of sulphuretted hydrogen in 1,000,000,000 of coal-gas, equivalent to approximately 1 grain of sulphuretted hydrogen in 600,000 cubic feet of coal-gas.

Having thus found the limit to which it could be detected by this means, an attempt was made to produce a standard set of colours corresponding to varying proportions of sulphuretted hydrogen.

Owing, however, to the extremely evanescent nature of the colour-spot, and to the difficulty of being sure the colours matched, this was abandoned in favour of what was found to be a more certain method.

By regulating the lead paper to a known distance from the nozzle, where the gas issues, and passing the gas at a half-foot per hour, it was found that the time required for the production of a colour was a constant for that proportion at that distance.

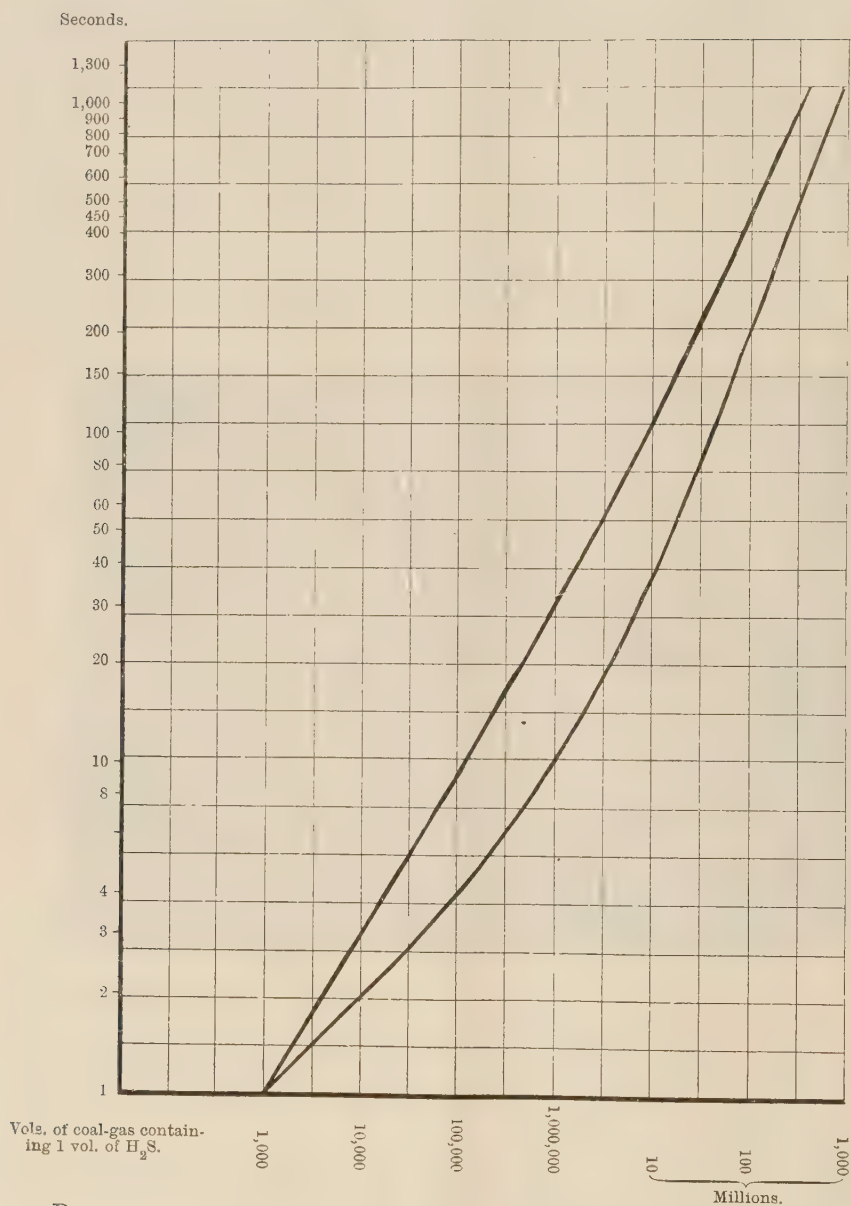


DIAGRAM SHOWING TIME REQUIRED TO DETECT VARYING QUANTITIES  
OF  $H_2S$  IN COAL-GAS.

The following table gives some of the mean results obtained by this method at different distances. The variation by different tests in any result was but slight.

| Time taken to produce a Colour Spot on Lead Paper by Gas containing One Volume of Sulphuretted Hydrogen in |                            |                                        |                                         |                                             |                                             |                                             |                                               |                                           |
|------------------------------------------------------------------------------------------------------------|----------------------------|----------------------------------------|-----------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|-------------------------------------------|
| Distance of Lead Paper from Nozzle at which Gas issues.                                                    | 1,000 volumes of Coal-Gas. | 10,000 volumes of Coal-Gas. min. secs. | 250,000 volumes of Coal-Gas. min. secs. | One million volumes of Coal-Gas. min. secs. | Ten million volumes of Coal-Gas. min. secs. | 100 million volumes of Coal-Gas. min. secs. | 1,000 million volumes of Coal-Gas. min. secs. | 10,000 million volumes of Coal-Gas. mins. |
| Close to...                                                                                                | at once                    | 0 2                                    | 0 5                                     | 0 8                                         | 1 7                                         | 5 0                                         | 11 30                                         | more than 30 mins.                        |
| $\frac{1}{8}$ inch ...                                                                                     | „                          | 0 4                                    | 0 10                                    | 0 15                                        | 1 30                                        | —                                           | —                                             | „                                         |
| $\frac{1}{4}$ inch ...                                                                                     | „                          | 0 8                                    | 0 15                                    | 0 30                                        | 1 50                                        | 12 0                                        | 21 30                                         | „                                         |
| $\frac{1}{2}$ inch ...                                                                                     | „                          | 0 12                                   | 0 18                                    | —                                           | 2 20                                        | —                                           | —                                             | „                                         |

Two curves have been plotted on the results obtained, the ordinates representing the number of volumes of coal-gas containing one volume of sulphuretted hydrogen and the abscissæ time in seconds. The ordinates are plotted in geometrical progression, it being obviously impossible to plot them as an arithmetical progression, and consequently time is plotted in the same manner. Two curves have been plotted in order to show the importance of the distance factor.

The right-hand curve represents the results found when the lead paper was close to the point of issue of the gas, and the left-hand curve the results obtained when the paper was adjusted to a distance of  $\frac{1}{4}$  inch from the nozzle.

#### DISCUSSION.

Mr. R. ORCHARD said that Dr. Rideal had experimented in a similar way to that described by Mr. Grimwood. In his experiment, using the gas referees' apparatus, Dr. Rideal had found that the delicacy of the official test was such that 1 part of sulphuretted hydrogen in five millions could be detected, passing 5 cubic feet of gas per hour. At first a gold-beater's skin balloon had been used. Subsequently a rubber balloon was tried, but it was found very difficult to free the rubber from sulphuretted hydrogen, and on allowing the apparatus to stand over-night, although on the previous evening the gas was free from sulphuretted hydrogen, after twelve to twenty-four hours a reaction was obtained from the rubber. The use of a rubber balloon had therefore been discontinued. Dr. Rideal had used a carboy with a large gold-beater's skin balloon in it, the carboy holding about 40 litres, and, using the official apparatus with six jets, he had found the minimum delicacy to be one in five millions.

Mr. HEHNER said that the delicacy of the sulphuretted hydrogen test by lead paper was exceedingly great. It was unintelligible why sulphuretted hydrogen must on no account be present in coal-gas, while from 17 to 22 grains per 100 cubic feet of other sulphur compounds were permitted, seeing that the sulphuretted hydrogen would burn into exactly the same product as the other sulphur compounds. The

nitro-prusside test, which was credited with being delicate, was a blunt test compared with the lead acetate test. *P*-amido-dimethylaniline gave a beautiful blue coloration (methylene blue) in the presence of sulphuretted hydrogen and ferric chloride, and had been recommended by Caro as a reagent for sulphuretted hydrogen. He (Mr. Hehner) had convinced himself that it was not nearly so delicate as lead acetate. Lead acetate solution was, again, much inferior to dry lead paper. Discoloration could be observed on the paper long before it was apparent in the solution. The preparation of mixtures of air or coal-gas with minute known amounts of sulphuretted hydrogen and the quantitative removal of the mixture from the vessel for the purpose of making the tests was by no means an easy one, as of course no substance or liquid could be used that might absorb the trace of sulphuretted hydrogen. While Mr. Dibdin had used an india-rubber balloon, by the expansion of which the gas was driven out, Dr. Rideal objected to the india-rubber on account of the difficulty with which the sulphuretted hydrogen that was absorbed by the balloon could again be driven out. Dr. Rideal had used gold-beater's skin instead. He (Mr. Hehner), however, found that the gold-beater's skin rapidly removed, probably on account of the oil with which the skin was prepared, every trace of sulphuretted hydrogen, both from air and from coal-gas, so that after a few hours' contact no  $H_2S$  was left. He had found it simplest to withdraw from a large vessel in which the gas mixture had been prepared by crushing calibrated capillary glass tubes filled with sulphuretted hydrogen, after allowing sufficient time for diffusion, some of the gas by the action of an aspirator or pump, measuring the gas thus withdrawn, under ordinary pressure. As to the general results, his experience was entirely in accordance with that of Mr. Dibdin.

Mr. GRIMWOOD, in reply, said that with regard to the question of the absorption of sulphuretted hydrogen by the india-rubber balloons and the subsequent giving of it up again, this has not been their experience.

When the apparatus was first put together they found that the rubber absorbed sulphuretted hydrogen, but after it had once had as much as it would take up, they had no further difficulty with it.

The mode of procedure certainly prevented the possibility of any occluded sulphuretted hydrogen affecting the result, as a blank determination was always made before any sulphuretted hydrogen was introduced into the apparatus.

With regard to the difference in sensibility found by Dr. Rideal and themselves, it must be remembered that two estimations of such difficulty as this cannot be expected to agree unless they are carried out under the same conditions, and it seems most probable that Mr. Hehner's experience of the absorption of sulphuretted hydrogen by the oil dressing of the gold-beater's skin, together with the difference in the two methods adopted, accounts for their want of agreement.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

### FOODS AND DRUGS ANALYSIS.

**Composition of Preserved Meats.**—Part 10 of Bulletin 13 of the United States Department of Agriculture, recently issued, is devoted to the examination of preserved meats. Very many analyses have been made. Boric acid was found in many instances and in a few cases benzoic acid. These have been added probably as sodium salts. Small amounts of tin and zinc were found in many samples, tin being the more abundant. The amount was rarely over 200 milligrammes per kilogramme, and generally much less. No lead is reported.

The text of the bulletin gives account of the processes of analysis, most of which are standard methods, but some special methods are published. The dictum of some authorities that 1 per cent. of glycogen calculated to the dry, fat-free meat indicates horse-flesh is declared incorrect. The results obtained by examination of the fats are found to be better guides as to the source of the meats. The following table of constants will be, therefore, of interest.

| Source of Fat.               |     | Canned<br>Roast-beef. | Canned<br>Corned-beef. | Canned<br>Smoked-beef. | Fresh<br>Horse-meat. |
|------------------------------|-----|-----------------------|------------------------|------------------------|----------------------|
| Melting-point (in °C.)       | ... | 36.5 to 43.9          | 37.2 to 43.4           | 37.7 to 43.1           | 27.2 to 32.5         |
| Chilling-point (in °C.)      | ... | 27.8 „ 37.0           | 29.0 „ 34.5            | 22.0 „ 29.0            | 12.0 „ 25.0          |
| Iodine number                | ... | 36.1 „ 50.6           | 37.9 „ 48.6            | 50.9 „ 57.5            | 61.4 „ 77.0          |
| Maumené number               | ... | 35.6 „ 36.0           | 35.5 „ 37.0            | —                      | 46.2 „ 56.5          |
| Degrees butyro-refractometer |     | 47.0 „ 55.5           | 52.7 „ 56.0            | 51.0 „ 58.5            | 55.2 „ 76.5          |

The method for boric acid was as follows: Fifty grammes of the meat are incinerated (complete combustion is not essential), transferred to a short-necked flask, and acidified with hydrochloric acid. The flask is connected with a condenser, and four or five portions of 20 c.c. each of methyl alcohol are distilled by means of a calcium chloride bath into sodium hydroxide. The distillate is evaporated to dryness to expel the methyl alcohol, care being taken that it is distinctly alkaline; the residue is dissolved in 20 c.c. of water, acidified with hydrochloric acid, heated to the boiling-point to expel carbonic acid, and then titrated by Thompson's method. Each c.c. of decinormal alkali corresponds to 0.0062 of boric acid.

For the determination of saltpetre, which was found in small amount in a number of samples, several methods are given. One of these is termed the picric acid method, depending on the well-known reaction between the nitrates and phenol-sulphonic acids, by which picric acid is formed, the amount being determined by colour comparison. The procedure recommended is as follows: 1 gramme of the sample is weighed into a 100 c.c. flask, 30 c.c. of water added, and heated on the water-bath for twenty minutes. Three c.c. of a saturated solution of silver sulphate are added for each per cent. sodium chloride present (previously ascertained), then 10 c.c. of lead subacetate solution and 5 c.c. of alumina cream, shaking after each addition. The mixture is made up to the mark with water, and filtered through a

fluted filter, returning the liquid until it passes clear. Twenty-five c.c. of the filtrate are evaporated to dryness, 1 c.c. of phenolsulphonic acid added, and mixed well with a glass rod, then 1 c.c. of water and a few drops of strong sulphuric acid, and the mass heated for a few minutes on the steam-bath, care being taken not to char it. The mass is washed into a Nessler cylinder by means of about 25 c.c. of water, made alkaline with ammonium hydroxide, and made up to 100 c.c. The amount of nitrate is determined by comparing this colour with that produced by solutions containing known amounts of nitrates treated in the same way.

The Bulletin recommends the use of a reagent obtained by dissolving 2.5 grammes of phenol, 2.5 c.c. of water, and 55 grammes of sulphuric acid. This gives a mixture of ortho- and para-phenol, and has been shown to give somewhat uncertain colour effects. Better results are obtained by using the phenol disulphonic acid obtained by mixing 3 grammes of phenol with 37 grammes of sulphuric acid, and heating the mixture for six hours in boiling water. The reagent thus obtained forms picric acid in the cold with nitrates, and gives more constant colour effects.

H. L.

**The Estimation of Sulphurous Acid in Dried Fruits.** A. Beythien and P. Bohrisch. (*Zeit. für Untersuch. der Nahr. und Genussmittel*, 1902, v., 401-409.)—The following quantities of sulphurous acid were found in various dried fruits (principally American), the results given being calculated into crystallized sodium sulphite ( $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ): Californian apricots, from 0.2162 to 1.1585 per cent.; Californian peaches, 0.9921 per cent.; Californian pears, 0.2399 per cent.; Italian prunes, 0.2637 per cent.; and "Görtzer" pears, 0.2901 per cent. The dried plums and apples examined were found to be free from sulphite. By cooking, less than one-half of the sulphite was removed from the fruits, and by soaking in water over-night and then cooking, a little more than one-half.

W. P. S.

**Estimation of Alkaloids in Cinchona Bark, etc.** F. de Myttenaere. (Reprint from *Bull. Acad. roy. de médecine de Belg., Séance of January 25, 1902*; through *Chem. Zeit. Rep.*, 1902, 118.)—The author has examined the methods which are official in the pharmacopœias of Austria (1893), Britain (1898), Germany (1900), Holland (1890), Italy (1892), and Switzerland (1893), as well as a process provisionally determined upon for the new Belgian volume; and he finds that they are all more or less faulty. He considers chloroform the only suitable solvent for the alkaloids, ammonia the best precipitant, and titration to be perfectly accurate. His own method is as follows: The sample is powdered till it will pass a sieve of 30 holes per linear centimetre; 7 grammes are then shaken at intervals for three hours in a 200 c.c. flask with 140 grammes of chloroform and 10 c.c. of 10 per cent. ammonia. Three grammes of gum tragacanth and 20 c.c. of water are next added, shaking thoroughly, and the vessel is rotated gently till the solid matter coheres. After standing one hour, 100 c.c. of the chloroform are quickly filtered off, the solvent removed by distillation, and the residue dried on the water-bath. It is taken up in

the minimum of chloroform, poured into a separating funnel which contains 15 c.c. of decinormal hydrochloric acid, the basin rinsed twice with 5 c.c. of chloroform and a third time with a sufficient quantity of ether to make the organic solution float. The whole is well shaken for five minutes, the acid liquor run off through a wet paper, and the ethereal liquid washed three times with 10 c.c. of water. The filter-paper is also washed, and the excess of acid is finally titrated with decinormal sodium hydroxide, using hæmatoxylin as indicator. The process is applicable to the tinctures and extracts of bark; the dry extract is first dissolved in dilute alcohol, and the solution evaporated to dryness with powdered pumice.

F. H. L.

### ORGANIC ANALYSIS.

**The Detection of Formaldehyde.** C. Arnold and C. Mentzel. *Zeit. für Untersuch. der Nahr. und Genussmittel*, 1902, v., 353-356.)—For the detection of formaldehyde in meat, butter, milk, etc., from 5 to 10 grammes of the substance are shaken out with 10 c.c. of alcohol and the alcoholic extract is filtered. To 5 c.c. of the filtrate are added 0.03 gramme of phenylhydrazine hydrochloride, 4 drops of ferric chloride solution, and 10 drops of concentrated sulphuric acid, keeping the solution cool during the addition. Should formaldehyde be present, the solution is coloured red, whilst in the absence of this preservative it remains yellow. Light-coloured beers may be tested directly after adding a little alcohol, the red colour produced when formaldehyde is present being easily seen in the froth formed on shaking. The coloration may also be shaken out with ether, the latter being then drawn off and placed in a small flask. On adding a little alcohol and a drop of concentrated sulphuric acid, the red colour is reproduced. The above method will detect one part of formaldehyde in 10,000.

W. P. S.

**The Analytical Constants of Neat's-foot, Tallow, and Horse Oils.** Augustus H. Gill and Allan W. Rowe. (*Journ. Amer. Chem. Soc.*, xxiv., 466.)—The authors have determined the various constants of a number of these oils, which are given in the following table:

|                 |   | Specific Gravity,<br>15° C. | Valenta,<br>0° C. | Maumené,<br>°C. | Specific Temp.<br>Reaction. | Iodine No. | Titre Test,<br>°C. | Iodine No.<br>Fatty Acid. |
|-----------------|---|-----------------------------|-------------------|-----------------|-----------------------------|------------|--------------------|---------------------------|
| Neat's-foot oil | 1 | 0.915                       | 70.0              | 42.2            | 87.9                        | 72.9       | 19.20              | 68.6                      |
| "               | 2 | 0.914                       | 75.5              | 42.2            | 87.9                        | 72.9       | 18.19              | 64.6                      |
| "               | 3 | 0.919                       | 51.0              | 49.5            | 103.1                       | 67.1       | 17.18              | 67.3                      |
| "               | 4 | 0.916                       | 61.5              | 42.2            | 87.9                        | 72.1       | 16                 | 69.5                      |
| "               | 5 | 0.916<br>(100° C.)          | 75.5              | 42.2            | 87.9                        | 66.0       | 25.5-26.5          | 63.6                      |
| Tallow oil      | 1 | 0.794                       | 73.5              | 35.0            | 72.9                        | 55.8       | 35.36              | 54.6                      |
| "               | 2 | 0.794                       | 71.0              | 35.0            | 72.9                        | 56.6       | 36.5-37.5          | 57.0                      |
| "               | 3 | 0.794                       | 75.7              | 35.0            | 72.9                        | 56.7       | 34.5-35.5          | 56.6                      |

## HORSE OILS.

| Colour, etc.                     | Specific Gravity<br>15° C. | Valenta,<br>0° C. | Mau-<br>mené,<br>0° C. | Specific<br>Temp.<br>Re-<br>action. | Iodine<br>No. | Iodine<br>No. of<br>Clear<br>Oil. | Titre<br>Test,<br>0° C. | Iodine<br>No.<br>Fatty<br>Acids. |
|----------------------------------|----------------------------|-------------------|------------------------|-------------------------------------|---------------|-----------------------------------|-------------------------|----------------------------------|
| 1. White-brown semi-fluid ...    | 0.919                      | 80.2              | 46.0                   | 95.8                                | 75.1          | —                                 | 32.5-33.5               | 72.9                             |
| 2. Dark-brown semi-fluid ...     | 0.916                      | 54.0              | 52.1                   | 108.5                               | 82.5          | 82.0                              | 30.0-31.0               | 72.3                             |
| 3. Yellow-brown liquid           | 0.922<br>(100° C.)         | 71.0              | 54.7                   | 114.0                               | 86.3          | 83.7                              | 25.0-26.0               | 78.7                             |
| 4. Golden-brown nearly solid ... | 0.798                      | 48.0              | 54.2                   | 112.9                               | 79.9          | 81.8                              | 30.31                   | 80.1                             |
| 5. Very like 4 ...               | 0.799                      | 61.0              | 53.5                   | 111.5                               | 78.8          | 78.2                              | 34.35                   | 82.1                             |

A. G. L.

**A Test for the Gumming Quality of Lubricating Oils.** Augustus H. Gill. (*Journ. Amer. Chem. Soc.*, xxiv., 467.)—The author has found that, in applying the elaidin test to mineral oils, those oils which deposit the most “tar” change the most in use, and a relation appears to exist between the amount of change (“tar”) and the oxygen absorbed. The gumming test was carried out by adding 11 grammes of Roth’s liquid (nitro-sulphuric acid) to 5 grammes of the oil and stirring thoroughly, the mixture being kept at a temperature of 10° to 15° C. The oxygen absorbed was determined by weighing out 5 to 10 grammes of the oil into a flask, drawing out the neck of the flask into a long, thin-walled capillary, and after allowing the flask to cool to 20°, sealing off the neck. The flask was then heated for 100 hours at 80° to 105°, allowed to cool to 20°, the capillary broken under water, and the quantity of water which entered determined, giving the quantity of oxygen absorbed.

A. G. L.

**Rubrescin, a New Indicator for Acid and Alkali Titration.** A. Rosenfeld and J. Silber. (*Farmazeft*, 1902, x., 263; through *Chem. Zeit. Rep.*, 1902, 130.)—Rubrescin is prepared by heating together 50 grammes of resorcinol and 25 grammes of chloral hydrate in an oil-bath at 160° C., when hydrochloric acid is split off. The melt is a brittle non-hygroscopic mass, soluble in hot amyl alcohol, in cold methyl and ethyl alcohols, in water; slightly soluble in ether; insoluble in chloroform. It is purified by powdering it and extracting with chloroform. Made up as a 1 per cent. solution, rubrescin yields a dark-red liquid, 3 to 6 drops of which, with 1 drop of decinormal sodium hydroxide and 100 c.c. of water, give a red colour which is permanent for one hour, and remains as a red fluorescence after one day. The same effect is produced by 1 or 2 drops of decinormal borax and di- and mono-sodium carbonate. One drop of decinormal sulphuric acid completely destroys the red colour produced by 3 drops of the indicator; with 5 or 6 drops the liquid becomes yellow.

Ammonia strikes a red colour with rubrescin also. Experiments on the value of this new indicator in presence of carbon dioxide and for alkaloidal work are in progress.

F. H. L.

## INORGANIC ANALYSIS.

**Electrolytic Separation of Lead from a Phosphoric Acid Solution.** A. F. Linn. (*Journ. Amer. Chem. Soc.*, xxiv., 435.)—The author shows that lead can be quantitatively separated by electrolysis from solutions of the phosphate in excess of phosphoric acid. The method pursued was to add to the lead solution, which should not contain more than 0.1 grammes of metal, 10 c.c. of sodium phosphate solution, and 12 to 14 c.c. of phosphoric acid (specific gravity 1.71), and then electrolyse for twelve to fourteen hours, using a current of  $N.D._{100} = 0.003$  ampère and voltage = 3. A smooth, uniform, gray coating is produced on the platinum dish which is washed first with water without interrupting the current, then very rapidly with a small quantity of absolute alcohol, and finally with ether, after which it is dried and weighed as metallic lead. If the current used is too strong, or if the electrolysis is continued too long, the deposit contains some phosphorus. If manganese is present in the solution some of it will be found with the lead, although manganese alone is not deposited from a solution of its phosphate in phosphoric acid.

A. G. L.

**The Volumetric Determination of Zinc.** E. Prothière. (*Journ. Pharm. Chim.*, 1902, xv., 419-422.)—The ordinary method of titrating the zinc with a standard solution of sodium sulphide suffers from the drawback that the lead acetate paper used as indicator reacts with the precipitated zinc sulphide.

Various attempts have been made to obviate this difficulty, but, according to the author, none of these are entirely satisfactory, and he therefore advocates the use of potassium antimony tartrate (tartar emetic) as an indicator in place of lead acetate.

Test paper impregnated with an aqueous 5 per cent. solution of tartar emetic gives no coloration until the whole of the zinc has been precipitated, when a yellow stain is instantly produced.

The test paper dried spontaneously in the air keeps well, and is very sensitive, giving a clear reaction with a solution of sodium sulphide containing 1 part in 10,000.

C. A. M.

**Volumetric Determination of Iron.** W. H. Gintl. (*Zeits. f. angew. Chem.*, 1902, xv., 398-402, 424-434.)—After discussing the various methods that have been proposed, the author describes experiments performed to investigate Storch's method, in which the iron solution is acidified with sulphuric acid, boiled for one and a half hours with metallic copper, and then titrated with permanganate. He found the results were always high in consequence of the formation of a small quantity of cuprous salt.

Excellent results were obtained by reducing with a spiral of palladium wire

impregnated with hydrogen. The palladium may be charged either by making it the cathode of an electrolytic cell, or by heating it and allowing it to cool in a current of hydrogen. The solution, containing up to 0.4 gramme  $\text{Fe}_2\text{O}_3$ , is placed in a flask, 4 c.c. of sulphuric acid are added, the palladium spiral (about 3 grammes in weight) is introduced, the flask is closed with a Bunsen valve and heated on a water-bath for one and a half hours. The palladium is then removed, and the solution is titrated with permanganate.

A. M.

**The Volumetric Estimation of Alumina, and Free and Combined Sulphuric Acid in Alums.** Alfred H. White. (*Journ. Amer. Chem. Soc.*, xxiv., 457.)—The author finds that if a solution of alum is titrated with barium hydrate solution in the presence of neutral potassium sodium tartrate, phenolphthalein being used as indicator, the quantity of barium hydrate required corresponds to the sulphuric acid combined with the alumina, plus the free sulphuric acid, the sulphuric acid present as alkaline sulphate not affecting the result. The tartrate is added to prevent precipitation of the alumina with consequent absorption of the pink colour. Precipitation of barium sulphate is also very considerably retarded. On the other hand, if sodium citrate is used instead of the tartrate, the barium hydrate required corresponds to the whole of the free acid, plus two-thirds of that combined with the alumina. The method is carried out as follows: 3 grammes of the alum are dissolved in 100 c.c. water. To 25 c.c. of this solution 50 c.c. of a neutral 10 per cent. potassium sodium tartrate solution are added; the solution is then titrated with barium hydroxide. Another 25 c.c. of the alum solution are evaporated to dryness on the water-bath; the residue is dissolved in 50 c.c. neutral 10 per cent. sodium citrate solution, allowed to stand for ten minutes, and titrated with barium hydroxide. The difference between the two titrations is equivalent to one-third of the sulphuric acid combined with alumina, and consequently to one-third of the alumina present. By multiplying this difference by three, and subtracting from the first value, the amount of free sulphuric acid is obtained. The barium hydroxide solution must be standardized against standard sulphuric acid solution in which approximately enough aluminium hydroxide has been dissolved to correspond to aluminium sulphate. The quantities of alumina found in this way are within 0.1 per cent. higher than those found gravimetrically.

The values for free acid found by this method are sometimes quite different from those found by the use of Beilstein and Grosset's method (*Bull. de l'Acad. Imp. des Sci.*, in St. Petersburg, 1890, 147), in which the free acid is extracted with alcohol after the addition of a large excess of ammonium sulphate to the saturated solution of the alum. It was found, however, that if the alum was directly dissolved in sodium citrate solution and the solution titrated at once, values similar to those given by this method were obtained. The explanation of these results lies in the fact that commercial alum is not always a homogeneous substance, often containing free acid in one part and basic salt in another. On solution, combination is only slowly effected. Beilstein and Grosset's method probably gives the amount of free acid present in the solid salt, but not the amount of free acid present in a solution of the salt which has been allowed to stand for some time.

A. G. L.

**The Determination of Lithia in Lepidolite.** W. J. Schieffelin and W. R. Lamar. (*Journ. Amer. Chem. Soc.*, xxiv., 392.)—Decomposition of the mineral is effected by means of the J. Lawrence Smith method, using a low red heat for the fusion. The ammonium salts should be slowly driven off from the alkalies, otherwise lithium chloride may be volatilized. Lithium is separated from the other alkalies, after the last traces of calcium have been precipitated by ammonium oxalate, by the Gooch method as follows: The solution of the chlorides is filtered into a flask of 80 c.c. capacity and evaporated down to 1 or 2 c.c. A few drops of water and 1 or 2 drops of hydrochloric acid are added to effect complete solution, and then 15 c.c. of amyl alcohol. The solution is then carefully heated to boiling, and kept gently boiling until all the water has been driven off. At this point a thermometer held in the vapour should read  $129^{\circ}$  to  $130^{\circ}$ . The amyl alcohol when cold is decanted through a filter into a platinum dish, and the residue washed till free from lithia, about 20 c.c. amyl alcohol being used. The solution is then evaporated to dryness at  $125^{\circ}$ ; 0.5 c.c. concentrated sulphuric acid is added to the residue, which is heated until the excess of acid has been volatilized, after which the sulphate is kept fused for one minute, covered, allowed to cool, weighed, again fused, and reweighed. The weight should be constant. The lithium sulphate obtained in this way is very nearly pure, rubidium and caesium chlorides being practically insoluble in amyl alcohol. For the small amounts of sodium and potassium chlorides dissolved, the Gooch correction of 0.0011 gramme for each 10 c.c. amyl alcohol, exclusive of washings, is made.

A. G. L.

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**The Presence of Barium in Mineral Waters containing Sulphates.** P. Carles. (*Ann. de Chim. anal.*, 1902, vii., 91-93.)—The author has found that the waters of Nérès-les-Bains contain lead, copper, barium, lithium, silico-fluorides, and boro-fluorides. As they were also found to contain sulphates and alkali bicarbonates, experiments were made to explain the simultaneous occurrence of barium and sulphuric acid.

In the neighbourhood of Nérès several quarries of fluorides and one of the mineral barytes are being worked. Several grammes of powdered barytes were boiled for three hours with water containing pure sodium bicarbonate. The liquid was then found to contain undecomposed barium sulphate and silico-fluoride, the excess of sodium bicarbonate, and the products of their reaction—viz., barium carbonate, and sodium sulphate and silico-fluoride.

On now supersaturating the liquid (suitably diluted) with carbon dioxide, it became clear within twelve hours, whilst both barium and sulphates were identified in the filtrate.

From this the author concludes that mineral waters containing sulphates and bicarbonates are capable of decomposing barium sulphate if they contain an excess of free carbon dioxide, with the formation of soluble barium bicarbonate; and he considers it probable that the lead in the waters of Nérès-les-Bains is due to a similar cause.

C. A. M.

**Preliminary Note on a New Separation of Thorium.** Floyd J. Metzger. (*Journ. Amer. Chem. Soc.*, xxiv., 275.)—Thorium is stated to be quantitatively precipitated from 40 per cent. alcoholic solutions by means of fumaric acid, which produces no precipitate in cold solutions of cerium, lanthanum, or didymium. Consequently, thorium can be quantitatively separated from these elements by means of fumaric acid, a single reprecipitation sufficing to remove the traces of these substances which may be carried down in the first precipitation. A. G. L.

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**A New Method of separating Ceria from Mixtures of Rare Earths.** R. J. Meyer and M. Koss. (*Berichte*, 1902, xxxv., 672-678.)—The following method is recommended by the authors for the rapid separation of cerium in a fairly pure condition. It is based upon the fact that cerium is precipitated from boiling solutions of ceric salts by magnesium acetate, whereas salts of lanthanum and didymium, etc., remain in solution.

In the case of a mixture of these earths the oxalates are converted into the compound ammonium nitrates, of which 100 grammes are dissolved in 2 litres of water in a large flask. The solution is heated to the boiling-point, and kept in motion by means of a current of steam, whilst a solution of 50 grammes of magnesium acetate in 500 c.c. of a 2.5 per cent. solution of hydrogen peroxide is introduced drop by drop, until a drop of the filtered liquid gives a pure white precipitate on treatment with ammonium hydroxide and hydrogen peroxide.

The liquid is then allowed to cool, and the orange-coloured precipitate of basic ceric acetate collected and washed with boiling water with the aid of a filter-pump, and dried at 120° C.

About 3 or 4 per cent. of didymium is simultaneously precipitated with the cerium salt, but the latter can readily be purified by dissolving it in nitric acid and converting it into ceric ammonium nitrate (*cf.* Wyruboff and Verneuil, *ANALYST*, xxiii., 164).

C. A. M.

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**Estimation of Silicon in Rich Ferro-Silicons by means of Peroxide of Sodium.** C. Ramovino. (*Moniteur Scientifique*, xvi., January, 1902; through *Chem. News*, lxxxv., 218.)—Half a gramme of the finely powdered ferro-silicon is mixed with 10 grammes of a mixture of sodium and potassium carbonates and 1 gramme of sodium peroxide, and the whole slowly heated in a platinum crucible over the blow-pipe. After decomposition is complete, the melt is allowed to cool, treated with boiling water and dilute hydrochloric acid in a porcelain dish, and the solution evaporated to dryness after adding 10 c.c. nitric acid and 2 grammes potassium chlorate. The residue is baked at 110°, taken up with 20 c.c. hydrochloric acid and 200 c.c. water, the solution boiled, filtered, and the insoluble residue ignited and weighed as silica. In the filtrate manganese and sulphur may be estimated. The method is especially applicable to those rich ferro-silicons which are not attacked by acids.

A. G. L.

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**Note on the Purification of Hydrochloric Acid from Arsenic.** L. T. Thorne and E. H. Jeffers. (*Proc. Chem. Soc.*, 1902, 118, [78].)—The hydrochloric acid to be purified is diluted with water until its specific gravity is 1.10, then raised to the boiling-point, and a piece of fine copper gauze introduced. The gauze should be of pure copper, of 100 meshes to the inch, and, for 2 litres of liquid, should be about four inches square, coiled very loosely round a long glass rod flattened at the end for convenience in handling. The whole is kept just boiling for one hour. If the gauze becomes blackened, it is replaced by a second, and, if necessary, a third piece. As soon as a piece of gauze remains bright after one hour's digestion, the acid is transferred to a retort without being allowed to cool, and distilled over another piece of gauze. As a precaution, the first 20 per cent. of the distillate are rejected, when 100 to 200 c.c. of arsenic-free acid are left in the retort. The method is simple, requires but little attention, and does not necessitate the use of the purest acid. The acid obtained is of constant boiling-point.

A. G. L.

**The Determination of Molybdic Acid after Reduction with Hydriodic Acid.** F. A. Gooch and O. S. Pulman, jun. (*Zeits. Anorg. Chem.*, xxix., 353.)—From 0.3 to 0.5 gramme of the sample of molybdate, at least 40 c.c. hydrochloric acid, and 0.2 to 0.6 gramme potassium iodide are placed in a flask of 150 c.c.

capacity, which is loosely closed by a bulb-tube (Fig. 1).

The solution is boiled down to a volume of 25 c.c., which can be read off by means of a mark on the flask, immediately diluted to 125 c.c., cooled, and transferred to a Drechsel's wash-bottle fitted with a trap (Fig. 2) containing potassium iodide solution. About 0.5 gramme manganous sulphate is then introduced to prevent the production of chlorine during the subsequent oxidation. Deci-normal potassium permanganate solution is then run in from a burette until it is in excess, and the volume used noted. A quantity of standard arsenious

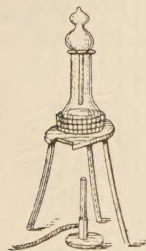


Fig. 1.



Fig. 2.

oxide solution, roughly equivalent to the permanganate used, is then added, after which a solution of 3 grammes tartaric acid and a small excess of potassium bicarbonate solution are added. Finally, the glass stopper and tubes are rinsed into the bottle, the contents of the trap are added, and the excess of arsenious oxide is titrated with iodine solution.

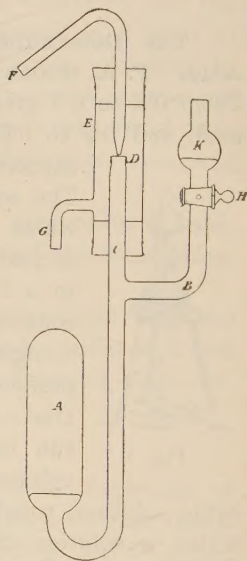
The amount of molybdic acid is given by the quantity of permanganate solution used plus that of the iodine solution, and minus that of the arsenious solution, one atom of oxygen being equivalent to two molecules  $\text{MoO}_3$ . The arsenious oxide is added to reduce the iodic acid, iodine, and higher oxides of manganese formed during the oxidation with permanganate. The oxidation can also be effected directly with iodine solution, but requires about two hours in that case, whereas with permanganate it is instantaneous. The test analyses given are satisfactory.

A. G. L.

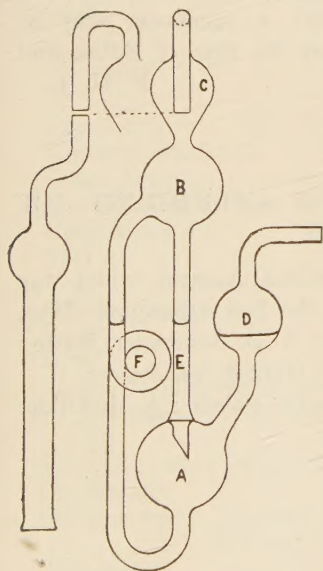
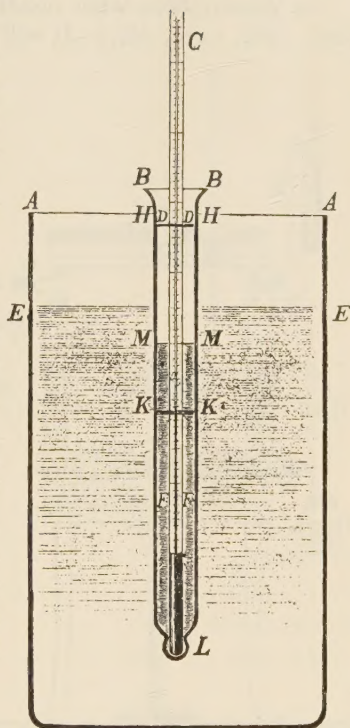
**Determination of Carbon in the Presence of Osmium. G. v. Knorre.** (*Zeits. f. angew. Chem.*, 1902, xv., 393.)—When osmium is heated in the presence of oxygen it forms the volatile tetroxide— $\text{OsO}_4$ —which is absorbed by potash solution just as carbon dioxide is. The gases can, however, be freed from osmium by passing them through a solution of ferrous sulphate. Acidified ferrous solution is placed in a flask, and the combustion gases are forced to bubble through it, after which they pass through an inverted condenser, then through a calcium chloride tube, and finally into potash bulbs. At the end of the operation the ferrous sulphate solution must, of course, be boiled. A. M.

### APPARATUS.

**Modified Form of Thermo-Regulator. T. S. Patterson.** (*Journ. Soc. Chem. Ind.*, 1902, xxi., 456.)—The bulb *A* is made from an ordinary test-tube, 6 inches by  $\frac{3}{4}$  inch, and is filled, as in the ordinary forms, with toluene (air would probably do as well for most purposes), which is sealed by mercury, as usual. Some inches above the top of the bulb *A* the side-tube *B* is fixed. This tube extends vertically upwards, and is fitted with the stopcock *H*, just above which a bulb *K* is blown. The other portion *C* of the tube ends at the same level as the bulb *K*, where it is slightly constricted. Mercury is introduced into both limbs *B* and *C* until it just appears about to overflow at *D*. The stopcock is then closed, and a piece of thin sheet rubber laid over the end *D* so as to touch the mercury, and then tied with a piece of thread. A wide piece of glass tubing *E*, open at both ends and fitted with a short side-tube *G*, is then fitted on a rubber cork, previously placed in position on the tube *C*. The upper end of *E* is closed by another rubber cork, through which passes the gas inlet tube *F*. This latter is tapered, as shown in the figure, and the end cut off with a very slight slant. The tapered end of the tube is pushed through the upper cork until it reaches to within about  $\frac{1}{2}$  a millimetre, or less, of the rubber membrane. The regulator is then ready for use. The gas-pipe is connected with *F*, and that to the burner with *G*. A small hole may be blown in *F* to act as a by-pass, or an external by-pass may be arranged if preferred. The temperature does not vary more than  $0.01^\circ$  in an hour. To adjust the apparatus, the bulb *A* is placed in the water-bath, the tap *H* opened, and the bunsen lit. The tap is closed when the water reaches a temperature  $0.3^\circ$  less than that actually required. A. M.



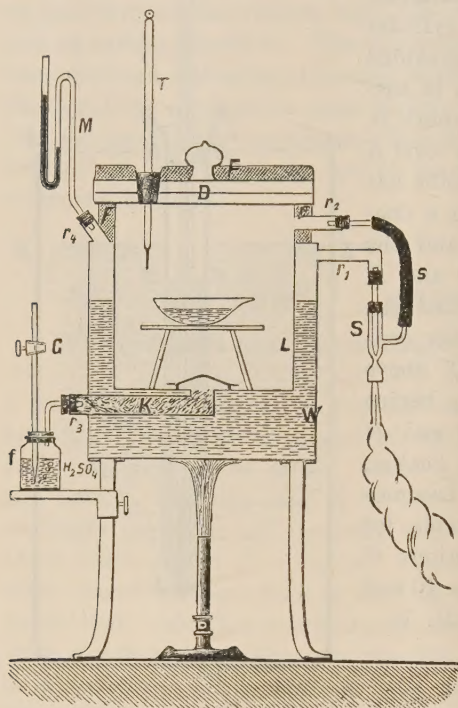
**A Melting-Point Apparatus.** A. Klinkhardt. (*Chem. Zeit.*, 1902, xxvi., 203.)—*B* is a glass cylinder weighted with mercury at the point *L*, and provided with a mark *H*. The thermometer, *C*, which is suspended in any convenient way, bears a special mark *D*, and is graduated in fifths. *B* is filled to the level *K* with the liquefied substance whose melting-point has to be ascertained, then fastened vertically in a convenient vessel containing ice-cold water, and the thermometer inserted so that the marks *D* and *H* coincide. When the material has solidified the whole apparatus is suspended inside a beaker containing water at a temperature of  $5^{\circ}$  or  $10^{\circ}$  above the melting-point expected. Directly melting begins to occur *B* falls slightly, and the marks *D* and *H* diverge; the apparatus is taken out of the beaker, and *C* is used as a stirrer until the mercury becomes stationary. The device is particularly suitable for determining the liquefying points of solutions of gelatin and glue, which may be employed as 20 and 10 per cent. solutions respectively. F. H. L.



**A New Design for Potash Bulbs.** J. N. Tervet. (*Chem. News*, lxxxv., 112.)—The advantages claimed for the potash bulbs shown in the figure are that the potash is used up more uniformly than in the ordinary pattern, that crystallization of potassium carbonate does not occur, and that owing to the intimate mixture of gas and solution the speed of absorption is increased, and, consequently, the time required for combustion is diminished.

The apparatus may be obtained from Max Kaehler and Martini, Berlin. A. G. L.

A Water-Oven with constant Current of Dry Air. W. Gallenkamp. (*Chem. Zeit.*, 1902, xxvi., 249.)—It will be seen from the accompanying illustration that this



oven is so constructed as to employ the steam raised in the jacket to work the injector *S*, whereby a steady current of air is extracted from the interior through the tube *s*. Air enters through the sulphuric acid bottle, the stream being regulated by the cock *G*; and in order to warm it before entering it is made to travel through the submerged tube *K* which is tightly packed with copper turnings. The cover is ground to fit, and carries a felt cover, *F*, to economize the heat. A pressure of 30 or 40 millimetres of mercury, indicated by the manometer *M*, suffices to work the injector. The apparatus may be fitted with a constant supply arrangement for the water; but in that case the inlet must be some 40 centimetres above the boiler level in order to establish the necessary pressure. A saline solution is advisable if a temperature of 100° is required. Liquids of higher boiling-points can also be employed in the jacket; if they are adopted, a condenser may be

fitted to the outlet of the injector. The oven is made by the firm of Böhm and Wiedemann, of Munich.

F. H. L.

#### EXAMINATION UNDER THE BUREAU OF MINES AMENDMENT ACT OF BRITISH COLUMBIA, 1899.

The half-yearly examination for the qualification of Provincial Assayer, which was held at <sup>Nelson</sup>Victoria, British Columbia, on April 22, 1902, and the four subsequent days, resulted in the following gentlemen being granted licenses: A. B. Rombauer, Butte; G. Crearer, Boundary Falls; L. E. Gooding, Rossland; C. Hunter, Vancouver.

The examiners were: H. Carmichael, Victoria; H. Harris, Nelson; A. McKillop, Nelson; J. Cuthbert Welch, Trail.